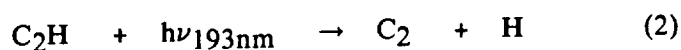
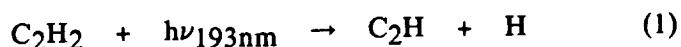


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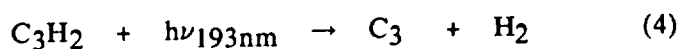
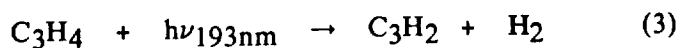
COMETARY IMPLICATIONS OF THE INTERNAL ENERGY DISTRIBUTIONS OF THE C₂ AND C₃ RADICALS PRODUCED IN THE PHOTOLYSIS OF THE C₂H AND C₃H₂ RADICALS; William M. Jackson, Yihan Bao, Randall S. Urdahl, Xueyu Song, Jai Gosine, and Chi Luu, Department of Chemistry, University of California, Davis, Ca. 95616

The C₂ and C₃ radicals are prominent emission in the visible region of cometary spectra. Observational evidence exist that suggest these radicals are formed as granddaughter fragments in the photolysis of more stable molecules. Likely candidates for these parent molecules are C₂H₂, C₃H₄ (allene) and CH₃C₂H (propyne). Recent laboratory studies have been done on all of these parent molecules and they indicate that they can indeed produce the observed cometary radicals. In the case of C₂H₂ the laboratory evidence suggest that C₂ is formed via that the following mechanism;



Evidence will be presented to show that the C₂ radical produced in the second reaction occurs in a variety of electronic, vibrational and rotational states. It will be argued that this is a result of conical intersections in the potential energy curves and the density of states associated with these curves. Since this is a property of the C₂H radical similar initial product state distributions are expected to occur in comets. This means that any models of the C₂ emission may have to start off with rotationally excited C₂ radicals in both the singlet and the triplet manifolds.

When C₃H₄ (allene) and CH₃C₂H (propyne) were photolyzed the C₃ radical is formed. In the allene case laboratory evidence shows that the C₃ radical is formed via the following mechanism;



More C₃ is formed in the case of allene than in the propyne case, even though the absorption cross section for propyne is a factor of 2 larger. This suggest that competing dissociation pathways are present during the photolysis of propyne that are not available to allene. The observed quantum state distributions of the C₃ product was the same for both parent molecules, indicating that the same intermediate state is involved. These observations can be understood if the excited propyne formed in the initial absorption step isomerizes to excited allene before it dissociates to the same daughter compound. This postulate has been tested by comparing RRKM calculations of the rate of isomerization of excited propyne versus the rate of decomposition to other products such as CH₃ + C₂H, and H + C₃H₃.

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